

09/914835

T 202.293.7060
F 202.293.7860

www.sughrue.com



SUGHRUE MION ZINN MACPEAK & SEAS, PLLC

September 4, 2001

BOX PCTCommissioner for Patents
Washington, D.C. 20231PCT/JP00/01170
-filed February 29, 2000

Re: Application of Kazuyuki SATO, Masamichi MORITA, Fumihiko YAMAGUCHI ✓
and Motonobu KUBO ✓
SURFACE TREATMENT AGENT COMPRISING ORGANIC-INORGANIC
HYBRID MATERIAL
Assignee: **DAIKIN INDUSTRIES, LTD.**
Our Ref: Q66019 ✓

Dear Sir:

The following documents and fees are submitted herewith in connection with the above application for the purpose of entering the National stage under 35 U.S.C. § 371 and in accordance with Chapter II of the Patent Cooperation Treaty:

- ☒ an English translation of the International Application.
- ☒ a Form PTO-1449 listing the ISR references, and a complete copy of each reference.

The Declaration and Power of Attorney, Assignment, will be submitted at a later date.

It is assumed that copies of the International Application, the International Search Report, the International Preliminary Examination Report, and any Articles 19 and 34 amendments as required by § 371(c) will be supplied directly by the International Bureau, but if further copies are needed, the undersigned can easily provide them upon request.

The Government filing fee is calculated as follows:

Total claims	<u>9</u>	-	<u>20</u>	=	<u> </u>	x	\$18.00	=	<u>\$0.00</u>
Independent claims	<u>3</u>	-	<u>3</u>	=	<u> </u>	x	\$80.00	=	<u>\$0.00</u>
Base Fee									<u>\$860.00</u>

TOTAL FEE \$860.00

A check for the statutory filing fee of \$860.00 is attached. You are also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880. The Commissioner is hereby authorized to charge any fees under 37 C.F.R. §§ 1.16, 1.17 and 1.492 which may be required during the entire pendency of the application to Deposit Account No. 19-4880. A duplicate copy of this transmittal letter is attached.

Priority is claimed from March 04, 1999 based on Japanese Patent Application No. 11/57100.

PCT/JP00/01170

09/914835

JC03 Rec'd POTATO 04 SEP 2001



Sughrue

SUGHRUE MION ZINN MACPEAK & SEAS, PLLC

Page 2
Q66019

Respectfully submitted,

Abraham J. Rosner
Registration No. 33,276

SUGHRUE, MION, ZINN,
MACPEAK & SEAS, PLLC
2100 Pennsylvania Avenue, N.W.
Washington, D.C. 20037-3213
Telephone: (202) 293-7060
Facsimile: (202) 293-7860
AJR/plr
Date: September 4, 2001

FOR THE "SECRET" 09/914835

DESCRIPTION

SURFACE TREATMENT AGENT COMPRISING ORGANIC-INORGANIC HYBRID MATERIAL

5

FIELD OF THE INVENTION

10 The present invention relates to a surface treatment agent comprising an organic-inorganic hybrid material to impart a superior stain block property to a substrate to be treated, such as a textile.

BACKGROUND OF INVENTION

15 Conventionally, various soil release treatment agents are suggested in order to impart water repellency, oil repellency and soil releasability to textiles (for example, carpets). USP 4,925,906, USP 5,015,259 and USP 5,223,340 disclose that soil release treatment agents comprising a copolymer containing carboxylic acid provide water repellency, oil repellency and soil releasability. Although water
20 repellency and oil repellency after cleaning are maintained using these copolymers, stain block property and soil releasability are not sufficiently maintained.

SUMMARY OF INVENTION

25 An object of the present invention is to provide a

0904433 14001
T03F01 5504060

treatment agent which imparts durability maintaining sufficient water repellency, oil repellency, stain block property, and soil releasability before and after cleaning.

The present invention provides a surface treatment agent, wherein, when a fiber for carpet is treated with the surface treatment agent, the treated fiber has following characteristics (1) and (2):

(1) a stain block property of at least 8, in the stain block examination according to AATCC-TM-175-1993;

(2) a Knoop hardness (KH) of the surface treatment agent of at least 5.

The present invention provides a surface treatment agent comprising;

(A) a metal alkoxide,

(B) a fluorine-containing compound having a functional group reactive with the metal alkoxide, and

(C) a reactive group-containing polymer having a reactive group reactive with a substrate to be treated.

Furthermore, the present invention provides a composition for an organic-inorganic hybrid material comprising:

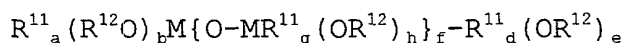
(A) a metal alkoxide,

(B) a fluorine-containing compound having a functional group reactive with the metal alkoxide,

(C) a reactive group-containing polymer having a reactive group reactive with a substrate to be treated.

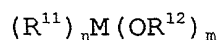
DETAILED DESCRIPTION OF THE INVENTION

5 The metal alkoxide (A) is hydrolysis polymerizing organometallic compound and has at least one alkoxy group. The metal alkoxide (A) may be a compound represented, for example, by the general formula:



10 wherein each R^{11} represents a methacryloxy group, an acryloxy group, a vinyl group-containing organic group, an alkyl group, a vinyl group, an aryl group or an epoxy group-containing organic group, and each R^{12} represents an alkyl group, an alkoxyalkyl group or an aryl group, and a is from 0 to 3, b is
15 from 0 to 4, $a+b = 2$ to 4, d is 1 or 0, e is 1 or 0, $d+e = 1$, f is from 0 to 10, for example, from 0 to 4, g is from 0 to 3, h is from 0 to 3, $g+h = 1$ to 3, and at least one from b, e and h is at least 1.

20 The metal alkoxide (A) may be a compound represented, for example, by the general formula:



 wherein R^{11} represents a methacryloxy group, an acryloxy group, a vinyl group-containing organic group, an alkyl group, a vinyl group, an aryl group or an epoxy group-containing organic group,
25 R^{12} represents an alkyl group, an alkoxyalkyl group or an aryl

group, and m is from 2 to 5, in particular 3 or 4, n is from 0 to 2, in particular 0 or 1, $m+n = 3$ to 5, in particular 4.

The number of alkoxy groups in the metal alkoxide (A) may be from 1 to 12, for example from 1 to 4.

5 The number of carbon atoms in the alkyl group (R^{11} and R^{12}) is, for example, from 1 to 6. The number of carbon atoms in the aryl group is, for example, from 6 to 18. The number of carbon atoms in the vinyl group-containing organic group and the epoxy group-containing organic group is, for example, from 10 2 to 6. Example of the vinyl group-containing organic group is an vinyl group. Example of the epoxy group-containing organic group is a glycidyl group. In the alkoxyalkyl group, the number of carbon atoms in the alkoxy group may be from 1 to 6, for example, and the number of carbon atoms in the alkyl group may be from 1 to 6. As examples of M (metal), silicon (Si), titanium (Ti), aluminium (Al), zirconium (Zr), tin (Sn) 15 and iron (Fe) are mentioned.

As examples of the metal alkoxide (A),
tetraethoxysilane $[\text{Si}(\text{OCH}_2\text{CH}_3)_4]$ (functionality of 4),
20 methyltriethoxysilane $[\text{CH}_3\text{Si}(\text{OCH}_2\text{CH}_3)_3]$ (functionality of 3),
dimethyldiethoxysilane $[(\text{CH}_3)_2\text{Si}(\text{OCH}_2\text{CH}_3)_2]$
(functionality of 2),
trimethylethoxysilane $[(\text{CH}_3)_3\text{SiOCH}_2\text{CH}_3]$ (functionality of 1),
and
25 ethoxysiloxane oligomer

[(CH₃CH₂O)₃Si-{O-Si(OCH₂CH₃)₂}_n-(OCH₂CH₃)]

(n = 1 ~ 4) (functionality of 6 to 12)

are mentioned.

The fluorine-containing compound (B) having functional
5 group reactive with the metal alkoxide may be, for example,

Rf-X

wherein Rf represents a fluoroalkyl group, X represents a
reactive group selected from the group consisting of a carboxyl
group or a sulfonic acid group or a salt thereof, a hydroxy group,
10 an epoxy group, a phosphoric group, an alkoxy silane group, a
halogenated silyl group, an isocyanate group and a blocked
isocyanate group.

The number of carbon atoms in the Rf group may be from 3
to 21, in particular, from 7 to 17. The Rf group (fluoroalkyl
15 group) may be CF₃(CF₂)_nCH₂CH₂- (n ≥ 0).

The fluorine-containing compound (B) may be, in
particular, Rf-OH or Rf-Si(OR²¹)₃,
wherein each R²¹ is independently a C₁₋₂₀ alkyl group.

The fluorine-containing compound (B) may be silane,
20 alcohol, chlorosilane, epoxy and phosphoric ester.

As examples of the fluorine-containing compound (B),
2-perfluorooctylethyltriethoxysilane

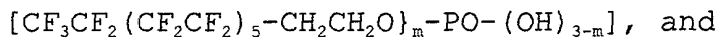
[CF₃CF₂(CF₂CF₂)₃CH₂CH₂-Si(OCH₂CH₃)₃],

2-perfluorodecylethyltriethoxysilane

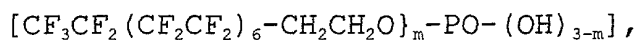
25 [CF₃CF₂(CF₂CF₂)₄CH₂CH₂-Si(OCH₂CH₃)₃],

- 2-perfluorododecylethyltriethoxysilane
 $[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_5\text{CH}_2\text{CH}_2-\text{Si}(\text{OCH}_2\text{CH}_3)_3],$
- 2-perfluorotetradecylethyltriethoxysilane
 $[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_6\text{CH}_2\text{CH}_2-\text{Si}(\text{OCH}_2\text{CH}_3)_3],$
- 5 2-perfluorooctylethanol $[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{OH}],$
 2-perfluorodecylethanol $[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_4\text{CH}_2\text{CH}_2\text{OH}],$
 2-perfluorododecylethanol $[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{OH}],$
 2-perfluorotetradecylethanol $[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_6\text{CH}_2\text{CH}_2\text{OH}],$
 2-perfluorooctylethyltrichlorosilane
- 10 $[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{CH}_2-\text{SiCl}_3],$
 2-perfluorodecylethyltrichlorosilane
 $[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_4\text{CH}_2\text{CH}_2-\text{SiCl}_3],$
 2-perfluorododecylethyltrichlorosilane
 $[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_5\text{CH}_2\text{CH}_2-\text{SiCl}_3],$
- 15 2-perfluorotetradecylethyltrichlorosilane
 $[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_6\text{CH}_2\text{CH}_2-\text{SiCl}_3],$
 3-perfluorooctyl-1,2-epoxypropane $[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_3-\text{Gly}],$
 3-perfluorodecyl-1,2-epoxypropane $[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_4-\text{Gly}],$
 3-perfluorododecyl-1,2-epoxypropane $[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_5-\text{Gly}],$
- 20 3-perfluorotetradecyl-1,2-epoxypropane $[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_6-\text{Gly}],$
 (Gly is a glycidyl group.)
- 2-perfluorooctylethylphosphate
 $[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_3-\text{CH}_2\text{CH}_2\text{O}\}_m-\text{PO}-(\text{OH})_{3-m}],$
- 2-perfluorodecylethylphosphate
- 25 $[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_4-\text{CH}_2\text{CH}_2\text{O}\}_m-\text{PO}-(\text{OH})_{3-m}],$

2-perfluorododecylethylphosphate



2-perfluorotetradecylethylphosphate



5 (m = 1 ~ 3)

are mentioned.

The amount of the fluorine-containing compound (B) may be from 0.1 to 50 parts by weight, for example, from 1.0 to 5.0 parts by weight, based on 100 parts by weight of the metal alkoxide (A).

The reactive group-containing polymer (C) having reactive group reactive with substrate is preferably a polymer which is obtained from a monomer having a carbon-carbon double bond and a reactive group. The reactive group in the reactive group-containing polymer (C) may be selected from the group consisting of a carboxyl group or a salt thereof, a hydroxy group, an epoxy group, a phosphoric group, an alkoxysilane group, an imine group, a sulfonic group, an amino group, an isocyanate group and a blocked isocyanate group. The reactive group may be, in particular, a carboxyl group or a sulfonic group or a salt thereof. A monomer constituting the reactive group-containing polymer may be a monomer in which the reactive group bonds to one carbon atom constituting the carbon-carbon double bond. As examples of the monomer constituting the reactive group-containing polymer, acrylic acid, methacrylic acid,

maleic acid, fumaric acid, citraconic acid, itaconic acid, styrenesulfonic acid and a sodium salt thereof are mentioned.

The reactive group-containing polymer (C) may be a hydroxy aromatic sulfonic acid or a condensate of carboxylic acid and formaldehyde.

The reactive group-containing polymer (C) can act as a stain block agent.

The amount of reactive group-containing polymer (C) may be from 0.001 to 10 parts by weight, for example, from 0.25 to 1.0 parts by weight, based on 100 parts by weight of the metal alkoxide (A).

The organic-inorganic hybrid material having a structure wherein a polymer is dispersed in a metal oxide (particularly MO_2 (M represents a metal atom))-containing three dimensional microstructural material (hereinafter abbreviated as microstructural material) is obtained from a composition for organic-inorganic hybrid material. The metal oxide (for example MO_2)-containing microstructural material is formed by hydrolysis and condensation by a sol-gel method of the metal alkoxide (A). An organic-inorganic hybrid material is formed wherein the fluorine-containing compound (B) and the reactive group-containing polymer (C) are dispersed in the metal oxide-containing microstructural material. The organic-inorganic hybrid material is suitable for the treatment agent for a textile, and at the same time has a superior stain block

property, transparency and hydrophobic property. A copolymer obtained from the metal alkoxide (A) and a polymerizable monomer (D) may be dispersed in the microstructural material. The organic-inorganic hybrid material preferably contains no inorganic fillers of at least 1 μm long.

It is believed that elements within the microstructural material are coupled by covalent bond, and that the fluorine-containing compound (B) and the reactive group-containing polymer (C) have hydrogen bonds within the microstructural material. It is believed that the metal atom in the metal alkoxide is bonded to the polymerizable monomer by a covalent bond.

In the treatment agent of the present invention, there may be contained a polymerizable monomer (D) which is copolymerized with the metal alkoxide (A). The polymerizable monomer (D) may be a monomer without a metal atom and/or a monomer with a metal atom. The polymerizable monomer (D) may be a radically polymerizable monomer. As examples of the monomer without metal atom (D1), methyl methacrylate, ethyl methacrylate, propyl methacrylate, n-butyl methacrylate, t-butyl methacrylate, phenyl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, t-butyl acrylate and phenyl acrylate are mentioned. As example of a metal in the monomer with metal atom (D2), silicon is mentioned. As examples of the monomer with metal atom (D2), 3-trimethoxy

504433-1-60
silyl propyl methacrylate, triethoxy silyl amide propyl
methacrylate, dimethylethoxy silyl methyl methacrylate and
trimethoxy silyl acrylate are mentioned. The amount of the
polymerizable monomer (D) may be from 0 to 200 parts by weight,
5 for example, from 50 to 100 parts by weight, based on 100 parts
by weight of the metal alkoxide (A) in the composition of the
present invention.

The organic-inorganic hybrid material is formed from an
organic component and an inorganic component. The organic
10 component comprises the fluorine-containing compound (B), the
reactive group-containing polymer (C) and the polymerizable
monomer without metal atom (D1). As examples of the inorganic
component, the metal alkoxide (A) and the polymerizable monomer
with metal atom (D2) are mentioned.

15 A coated film of the organic-inorganic hybrid material
is formed on a base material. The base material may be a polymer
substance. The base material may be, for example, in the form
of a film, a fiber and a cloth. The coated film of an
organic-inorganic hybrid material may comprise a dense layer,
20 and an uneven layer which is formed combinedly onto the dense
layer wherein the whole surface is roughened with microscopic
unevenness formed on the dense layer. Thickness of the coated
film may be from 0.01 to 100 μm .

The Knoop hardness (KH) of the coated film formed from
25 the organic-inorganic hybrid materials is at least 5. The Knoop

hardness, for example, may be at least 6, in particular, at least 8. The Knoop hardness is measured by means of Terasawa type microhardness meter (SM-2 manufactured by Taiyo Tester Co., Ltd.).

5 The organic-inorganic hybrid material may have a contact angle of water of at least 100 degree.

05914835-121301
10 The metal alkoxide (A), the fluorine-containing compound (B), the reactive group-containing polymer (C) and, if required, the polymerizable monomer (D) are hydrolyzed in an aqueous medium in the presence of a catalyst (for example, an acid or a base), and a hydrolysed product (that is, the organic-inorganic hybrid material) is obtained. The hydrolysed product is dissolved or dispersed in a medium (water or organic solvent), then an initiator (if required, a crosslinking agent)
15 is added to give a hybrid material/medium mixture. As examples of the organic solvent, alcohols (for example, methanol and ethanol), ethers (for example, benzoin methyl ether) and amides (for example, N,N-dimethylformamide) are mentioned. As examples of the initiator, photo initiators (for example, benzoin methyl ether), peroxides (for example, ammonium
20 peroxodisulfate, ammonium persulfate) are mentioned. As examples of the crosslinking agent, bis-acrylamides (for example, N,N-methylene-bis-acrylamide) are mentioned. An emulsifier, a pH adjuster and the like may be employed in order
25 to disperse the organic-inorganic hybrid material in water.

Any of the following emulsifiers may be employed;
for example, anionic surface active agents such as an alkyl
sulfate ester salt, an alkyl aryl sulfate ester salt, an alkyl
phosphate ester salt, a fatty acid salt;

5 cationic surface active agents such as a alkylamine salt and
a quaternary alkyl amine salt;

nonionic surface active agents such as a polyoxyethylene alkyl
ether, a polyoxyethylene alkyl aryl ether and a block-type
polyether; and

10 ampholytic surface active agents such as a carboxylic acid type
agent (for example, amino-acid type, betaine type, etc) and a
sulfonic acid type agent. These emulsifiers may be employed
independently or two or more of them may be employed in mixture.

In the case wherein the treatment agent contains an acidic
15 group such as a carboxyl group or a carboxylic acid, it is
preferable to adjust pH by adding at least one basic compound
after condensation polymerization of the metal alkoxide (A),
the fluorine-containing compound (B) having functional group
reactive with the metal alkoxide and the reactive group-
20 containing polymer (C) having reactive group reactive with
substrate to be treated. In the case wherein the treatment
agent has a basic group such as an amino group or an amine imide
group, it is preferable to adjust pH by adding at least one acidic
compound after condensation polymerization of the metal
25 alkoxide (A), the fluorine-containing compound (B) having

functional group reactive with the metal alkoxide and the reactive group-containing polymer (C) having reactive group reactive with substrate to be treated. In the case where the treatment agent has the above-mentioned acidic group and the above-mentioned basic group, the hydrophilic property of the resultant copolymer is enhanced, and the dispersibility of the polymer can be improved, by adjusting pH by way of adding at least one acidic compound or at least one basic compound depending on the content of these groups, after condensation polymerization of the metal alkoxide (A), the fluorine-containing compound (B) having functional group reactive with the metal alkoxide and the reactive group-containing polymer (C) having reactive group reactive with substrate to be treated.

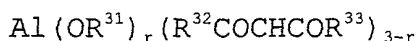
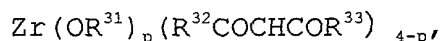
As examples of the above-mentioned basic compound, amines such as ammonia, methylamine, dimethylamine, trimethylamine, ethyl amine, diethylamine, triethylamine, ethanolamine, diethanolamine, dimethyl amino ethanol; alkali metal hydroxides such as potassium hydroxide and sodium hydroxide are mentioned. In addition, as examples of the above-mentioned acidic compound, inorganic acid such as hydrochloric acid, phosphoric acid, sulphuric acid and nitric acid; and organic acids such as formic acid, acetic acid, propionic acid, lactic acid, oxalic acid, citric acid, adipic acid, (meth)acrylic acid, maleic acid, fumaric acid and itaconic acid are mentioned. The pH value adjusted may be

usually from 6 to 10, more preferably from 7 to 10.

Although the aqueous medium in the aqueous dispersion essentially consists of water, in some cases an organic solvent such as alcohols may be contained up to approximately several percentage by weight.

In the present invention, it is preferable to employ the following metal chelate compound (E) and β -keto compound (F).

The metal chelate compound (E) comprises at least one metal chelate compound and/or partially hydrolysed compound thereof selected from the group consisting of the compounds represented by the following general formulas:



wherein R^{31} and R^{32} are, the same or different, an alkyl group having 1 to 6 carbon atoms, and R^{33} is an alkyl group having 1 to 5 carbon atoms or an alkoxyl group having 1 to 16 carbon atoms.

It is believed that the metal chelate compound (E) performs a function of accelerating a condensation reaction during the condensation polymerization of the metal alkoxide (A), the fluorine-containing compound (B) having functional group reactive with the metal alkoxide and the reactive group-containing polymer (C) having reactive group reactive with the substrate to be treated.

In each of the formulas representing the metal chelate compound (E), the alkyl group R^{31} and R^{32} having 1 to 6 carbon atoms may be a linear or branched alkyl group such as a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, a t-butyl group, an n-pentyl group and an n-hexyl group. For the R^{33} group, the alkyl group having 1 to 5 carbon atoms may be a linear or branched alkyl group such as a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, a t-butyl group, an n-pentyl group and an n-hexyl group, and the alkoxyl group having 1 to 16 carbon atoms may be a methoxy group, an ethoxy group, an n-propoxy group, an isopropoxy group, a n-butoxy group, an isobutoxy group, a sec-butoxy group, a t-butoxy group, a lauryl group and a stearyl group. In the case wherein the compound in each of the above-mentioned formulas has two or more of R^{31} , R^{32} and/or R^{33} groups, they may be the same or may be different from each other.

As examples of the metal chelate compound (E), zirconium chelate compounds such as zirconium tri-n-butoxy ethyl acetoacetate, zirconium di-n-butoxy bis(ethyl acetoacetate), zirconium n-butoxy tris(ethyl acetoacetate), zirconium tetrakis(n-propyl acetoacetate), zirconium tetrakis(acetyl acetoacetate) and zirconium tetrakis(ethyl acetoacetate); titanium chelate compounds such as titanium diisopropoxy

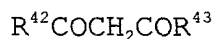
09914835-121801
bis(ethyl acetoacetate), titanium diisopropoxy bis(acetyl
acetoacetate) and titanium diisopropoxy bis(acetyl acetate);
aluminum chelate compounds such as aluminum diisopropoxy ethyl
acetoacetate, aluminum diisopropoxy acetyl acetate, aluminum
5 isopropoxy bis(ethyl acetoacetate), aluminum isopropoxy
bis(acetyl acetate), aluminum tris(acetyl acetate), aluminum
tris(ethyl acetoacetate) and aluminum monoacetylacetate
bis(ethyl acetoacetate) are mentioned.

Among the above-mentioned metal chelate compounds (E),
10 zirconium tri-n-butoxy ethyl acetoacetate, titanium
diisopropoxy bis(acetyl acetate), aluminum diisopropoxy ethyl
acetoacetate and aluminum tris(ethyl acetoacetate) are
preferable. In the present invention, the metal chelate
compound (E) may be employed independently or two or more of
15 them may be employed in mixture.

The blending ratio of the metal chelate compound (E) is
usually from 0.01 to 50 parts by weight, preferably from 0.1
to 50 parts by weight, more preferably from 0.5 to 10 parts by
weight, based on 100 parts by weight of the metal alkoxide (A).
20 Soil releasability is further improved by employing the metal
chelate compound (E) by using the above-mentioned blending
ratio.

The β -keto compound (F) comprises at least one compound
selected from β -diketones and/or β -keto esters represented by
25 the following general formula, and provides a function of

storage stabilizer for the surface treatment agent of the present invention;



wherein R^{42} and R^{43} are the same as R^{32} and R^{33} respectively in the above-mentioned each general formula representing the metal chelate compound (E).

In detail, it is believed that the β -keto compound coordinates with the metal atom in the metal chelate compound (E) when an aqueous dispersion is prepared and it suitably prevents the acceleration function of the metal chelate compound for the condensation reaction of the metal alkoxide (A), the fluorine-containing compound (B) having functional group reactive with metal alkoxide and the reactive group-containing polymer (C) having reactive group reactive with substrate to be treated, and at the same time it further stabilizes the resultant composition during storage.

As examples of the β -keto compound (F), acetylacetone, methyl acetoacetate, ethyl acetoacetate, n-propyl acetoacetate, isopropyl acetoacetate, n-butyl acetoacetate, isobutyl acetoacetate, sec-butyl acetoacetate, t-butyl acetoacetate, 2,4-hexanedione, 2,4-heptanedione, 3,5-heptanedione, 2,4-octanedione, 3,5-octanedione, 2,4-nonanedione, 3,5-nonanedione and 5-methyl-2,4-hexanedione are mentioned. Among above-mentioned β -keto compounds (F), acetylacetone and ethyl acetoacetate are preferable. In the

present invention, the β -keto compound (F) may be employed independently or two or more of them may be employed in mixture. A blending ratio of β -keto compound (F) is at least 2 moles, preferably from 3 to 20 moles, more preferably from 4 to 15 moles, based on 1 mole of the metal chelate compound (E).

The aqueous dispersion of the surface treatment agent of the present invention may comprise the metal chelate compound (E) and the β -keto compound (F) and, if required, may comprise other additives. In detail, at least one colloidal silica and/or colloidal alumina (hereinafter collectively referred to as "colloidal additive (G)") may be added in order to improve a soil releasability of fiber. The above-mentioned colloidal silica is a dispersion wherein a high-purity silicic anhydride is dispersed in water and/or hydrophilic organic solvent. An average particle diameter of the colloidal silica is usually from 5 to 100 nm and preferably from 10 to 50 nm, and solid concentration is usually approximately from 10 to 40 % by weight.

As examples of the colloidal silica, Snow tex, methanol silica sol, isopropanol silica sol (manufactured by Nissan Chemical Industries, Ltd.) are mentioned. The above-mentioned colloidal alumina is an alumina sol in aqueous dispersion medium with pH of from 2.5 to 6 or an alumina sol in a hydrophilic organic solvent dispersion medium. The average particle diameter of the colloidal alumina is usually from 5 to 200 nm, preferably

from 10 to 100 nm, and the solid concentration is usually approximately from 5 to 25 % by weight. As alumina, for example, synthetic alumina, boehmite and pseudo boehmite may be employed. Colloidal aluminas of this type are commercially available with trade names such as ALUMINA SOL-100, ALUMINA SOL-200, ALUMINA SOL-520 (manufactured by Nissan Chemical Industries, Ltd.). In the present invention, the colloidal additive (G) may be employed independently or two or more of them may be employed in mixture. A blending ratio of colloidal additive (G) is usually at most 30 parts by weight, preferably at most 20 parts by weight as solid content, based on 100 parts by weight of the treatment agent.

After the hybrid material/medium mixture is applied on the surface of a base material, a curing process may be applied. The curing may be performed by means of light (for example, UV irradiation) or heat (for example, application of heat of from 100 to 150 °C) etc.

An organic-inorganic hybrid materials of the present invention (the surface treatment agent) may be applied to a base material (that is, a substrate to be treated) by a conventionally known method. The surface treatment agent is usually diluted with an organic solvent or water and deposited on the surface of the substrate to be treated (for example, carpet) by known methods such as a dipping application, a spray coating application and a foam coating application. If

necessary, a carpet base fabric or a carpet yarn may be processed with steam before the application of the treatment agent. It may be applied along with a suitable crosslinking agent followed by curing. Other treatment agents such as water repellents and oil repellents, moth proofing agents, softening agents, antimicrobial agents, flame retardants, antistatic additives, coating fixing agents and crease resistant agents may be added to the surface treatment agent of the present invention and the resultant treatment reagent mixtures may be applied. In the case of the dipping application, a concentration of the organic-inorganic hybrid material in a dipping liquid may be from 0.05 to 30 % by weight. In the case of the spray application, the concentration of the organic-inorganic hybrid material in the treatment liquid may be from 0.1 to 5 % by weight.

The substrate to be treated with the surface treatment agent of the present invention may be a textile. It is especially preferable that the substrate is a carpet. Various examples may be mentioned as the textile. As examples of the textile, vegetable fibers and animal fibers such as cotton, hemp, sheep wool and silk, synthetic fibers such as polyamide, polyester, polyvinylalcohol, polyacrylonitrile, polyvinyl chloride and polypropylene, semi-synthetic fibers such as rayon and acetate, inorganic fibers such as fiberglass, carbon fiber and asbestos fiber or mixture of these above-mentioned fibers are mentioned. Superior resistance against a cleaning solvent

and mechanical brushing of the present treatment agent enables the treatment agent of the present invention preferably to be applied for carpets of nylon and polypropylene.

The textile may be in any form such as a fiber, a thread
5 or a cloth. In the case where the carpet is treated with the surface treatment agent of the present invention, the carpet may be manufactured from fibers or yarns after the fibers or the yarns were treated with the surface treatment agent. Alternatively, an already prepared carpet may be treated with
10 the surface treatment agent.

As the substrate to be treated with the surface treatment agent of the present invention, glass, paper, wood, leather, fur, asbestos, brick, cement, metal, building stone, concrete, oxide, ceramics, plastics, painted surface and plaster may be
15 mentioned, in addition to the textile.

The treatment agent for substrate to be treated, except the textile, (for example, wood, metal, stone, plastics, concrete, glass) may comprise the metal alkoxide, the fluorine-containing compound having functional group reactive
20 with the metal alkoxide, and the reactive group-containing polymer having reactive group reactive with substrate to be treated.

For example, in the case that the treatment agent is used as a mold releasing agent and a resin adhesion inhibitor, a hard
25 coated film having low surface free energy is formed on a surface

of a metal. As a result, the mold releasability of the formed resin material from a mold is improved and the adhesion between the mold surface and the resin material is prevented, in addition to the impartation of water repellency and oil repellency.

EXAMPLES

The present invention will be illustrated hereinafter by showing Examples and Comparative Examples, but these example are not intended to be any limitation of the present invention.

The term "part" represents part by weight, unless specified.

The examinations were performed as follows.

Knoop hardness

A coated film of an organic-inorganic hybrid material (thickness: 1 μ m) is formed on a glass plate. A Knoop hardness of the coated film is measured by Terasawa type microhardness meter (SM-2 manufactured by Taiyo Tester Co., Ltd.).

Water repellency

A little drop of isopropyl alcohol/water mixture liquid having the composition shown in Table I is gently placed on a surface of a carpet fabric. Water repellency is represented by a maximum content of isopropyl alcohol in the mixture liquid wherein a drop shape is kept after three minutes.

Table I

Mixture composition (volume ratio %)	
Isopropyl alcohol	Water
60	40
50	50
40	60
30	70
20	80
10	90
0	100

Oil repellency

Oil repellency is evaluated by means of AATCC-TM-118-
 1966. Several drops (diameter 4 mm) of a test liquid shown in
 Table II are placed on 2 points of sample cloth. After 30
 seconds, the drop penetration state of the drops is observed.
 The highest number of the oil repellency given by the
 examination liquid that does not exhibit the penetration is
 expressed as the oil repellency.

Table II

Oil repellency	Test liquid	Surface tension (dynes/cm at 25 °C)
8	n-Heptane	20.0
7	n-Octane	21.8
6	n-Decane	23.5
5	n-Dodecane	25.0
4	n-Tetradecane	26.7
3	n-Hexadecane	27.3
2	Mixture liquid of 35 parts of hexadecane and 65 parts of nujol	29.6
1	Nujol	31.2
0	Inferior to 1	---

Stain block (SB) property

The evaluation of the SB property was performed by the following method according to AATCC-TM-175-1993.

5 After the carpet fabric is cut into 11 cm x 11 cm pieces and kept to stand for at least 4 hours in a constant humidity thermostat (21 °C, 65% RH), the fabric is stained by soaking with a staining liquid containing an acid dye.

10 Specifically, a ring is placed with about 1 kg load on a treated surface of the carpet piece treated with a treatment agent. 20 ml of a staining liquid prepared in the way that 100 ± 1 mg of Red 40 is dissolved in 1 liter pure water followed by pH adjusting to pH 2.8 ± 0.1 with citric acid is poured into this ring, and then a cup having about 2 kg load is urged to
15 the stained area of the carpet piece five times. Then after the carpet piece is kept to stand in a constant humidity thermostat (21 °C, 65% RH) for 24 hours, the carpet piece is rinsed with running water until the rinse water is clear. The SB property is evaluated with a visual observation estimate by
20 using a stain scale.

Soil releasability

Soil releasability of a carpet treated with a surface treatment agent is evaluated with the following method according to AATCC-TM-123-1995.

25 After the carpet fabric is cut into 5.5cm x 8cm pieces

and kept to stand for 4 hours in a constant humidity thermostat (21 °C, 65% RH), the fabric is stained with dry soil which has the following composition and sufficiently dried.

Specifically, five pieces of the treated carpet are placed under the state that a back surface of each piece is attached to an internal of a ball mill so that the treated surface of the piece is upside. 0.031g of dry soil (dry soil was totally 6.82g for five pieces) and 50 ceramic balls (diameter of 2.0cm) are placed in the ball mill, per surface area 1cm² of carpet piece. The ball mill is rotated with 80 rpm for 7 minutes 30 seconds, and the dry soil is adhered to the carpet piece surface uniformly.

The ball mill employed here is cylindrical, and has a inside bottom diameter of 12.0 cm and a height of 9.5 cm. Then excessive dry soil adhered to the surface is removed thoroughly with a home vacuum cleaner. A color difference (ΔE) of the carpet surface is measured using a color-difference meter (MINOLTA CR-310), and a soil releasability ratio is calculated by the following equation.

$$\text{Soil releasability ratio (\%)} = 100 \times (\Delta E_N - \Delta E_{Tn}) / \Delta E_N$$

ΔE_N : Color difference of untreated carpet after soil releasability evaluation

ΔE_{Tn} : Color difference of carpet treated with surface

treatment agent after soil releasability evaluation (n: number of cleaning)

The composition of the dry soil is as follows.

5 Table III

Components	Weight ratio (%)
Peat moss	38.4
Cement	18
Kaolin	18
Silica	18
Carbon black	1.15
Ferric oxide (III)	0.30
Nujol	6.25

Lab value is L: from 25 to 31, a: from 2.3 to 2.6, b: from 4.2 to 4.8.

Fluorine residual ratio

10 Fluorine residual ratio of a carpet treated with a surface treatment agent is determined by the following method. Two hundred mg of carpet pieces before and after cleaning are collected and processed by an oxygen flask combustion method. F⁻ (a fluorine ion) is absorbed in water which is absorption liquid. Then the amount of F⁻ (fluorine ion) is calculated by
15 a fluorine ion electrode method to give a fluorine residual ratio.

Cleaning method

The carpet fabric treated with the surface treatment agent is cleaned according to a method of AATCC-TM-138-1992, and it is cleaned. The details of the cleaning are as follows.

5 A surface of a carpet piece cut into 11cm × 11cm square is rinsed with running water at 50 °C for one minute and squeezed with mangles (pressure 5mg/cm²). The carpet piece is fixed on a sample pedestal of a cleaning testing machine (STAIN & CLEANING TESTER manufactured by Yoshida Seiki Seisakusyo
10 Company) described in JIS L1023-1992 so that a rotating brush rubs the carpet pile. One percent sodium lauryl sulfate aqueous solution (SLS) (adjusted at pH 8 with NaOH aqueous solution) (5.6 ml) adjusted at 50 °C is poured onto a carpet piece with a pipet. The rotating brush and the sample pedestal are rotated
15 and the carpet piece is cleaned. The operation wherein the sample pedestal rotates in regular direction five revolutions, in reverse direction five revolutions, in regular direction five revolutions, and then in reverse direction five
20 revolutions (during the rotation of the sample pedestal rubbing by the rotating brush is continued) is defined as one set of cleaning.

In the cleaning test, the cleaning operation is repeated five sets without adding 1% aqueous SLS solution.

25 In addition, the sample pedestal rotates at 20 rpm, the brush rotates at 240 rpm, and vacuum and water spray nozzle of

the cleaning testing machine are not employed.

The test carpet piece is thoroughly rinsed with running water at 50 °C, squeezed with mangles and dried in a hot-air drier at 105 °C for 30 minutes.

5 Synthesis Example 1

10 In a 100ml flask equipped with a stirrer, a thermometer and a dropping funnel, 15 parts of polymethacrylic acid (PMA) aqueous solution having a solid concentration of 0.5 % by weight and a pH value adjusted to pH 2.0 by adding 10 % by weight sulfamic acid aqueous solution (a stain blocking agent, FX-668F manufactured by 3M Company), 1.5 parts of heptadecafluoro-1,1,2,2-tetrahydrodecyl triethoxy silane [$\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{-Si}(\text{OCH}_2\text{CH}_3)_3$] (a fluorine-containing compound) (manufactured by Shin-Etsu Chemical Co., Ltd.) and 5 parts of methyl methacrylate

15 (MMA) were added into 15 parts of 3-methacryloxypropyl trimethoxy silane [$\text{CH}_2=\text{CH}(\text{CH}_3)-(\text{C}=\text{O})-\text{O}-(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$] (TMSM) (manufactured by Shin-etsu Chemical Co., Ltd.) and 15 parts of tetraethoxysilane [$\text{Si}(\text{OCH}_2\text{CH}_3)_4$] (TEOS) (manufactured by Shin-etsu Chemical Co., Ltd.). The mixture was stirred at room

20 temperature for one hour and hydrolysis and condensation polymerization reactions were performed. Resultant compound was named Product 1.

Synthesis Example 2

25 The same procedure as in Synthesis Example 1 was followed to give Product 2 except that 1.5 parts of 2-(perfluoro

octyl)ethanol $[F(CH_2)_8CH_2CH_2OH]$ was used instead of 1.5 parts of heptadecafluoro-1,1,2,2-tetrahydrodecyl triethoxy silane.

Comparative Synthesis Example 1

5 The same procedure as in Synthesis Example 1 was followed to give Product 3 except that 30 parts of methacrylic acid was used instead of 15 parts of 3-methacryloxypropyl trimethoxy silane and 15 parts of tetraethoxysilane.

Comparative Synthesis Example 2

10 The same procedure as in Synthesis Example 1 was followed to give Product 4 except that 1.5 parts of n-decyl triethoxy silane instead of 1.5 parts of heptadecafluoro-1,1,2,2-tetrahydrodecyltriethoxy silane, and 15 parts of a polymethyl methacrylate solution in acetone/water mixture having a solid concentration of 0.5 % by weight instead of 15 parts of
15 polymethacrylic acid (PMA) aqueous solution having a solid concentration of 0.5 % by weight were used.

Preparative Example 1

Preparation of Product 1/MMA cross-linking precursor (Solution A)

20 Product 1 provided with Synthesis Example 1, methanol, benzoin methyl ether, N,N-methylene bis acrylamide were mixed in the amounts shown in Table A to give a Product 1/MMA cross-linking precursor (Solution A).

Preparative Example 2

25 Preparation of Product 2/MMA cross-linking precursor (Solution

B)

The same procedure as in Preparative Example 1 was followed to give Product 2/MMA cross-linking precursor (Solution B) except that Product 2 was used instead of Product 1 used in the Preparative Example 1.

Preparative Example 3

Polymerization of Product 1/MMA copolymer (Solution C)

Product 1 provided with Synthesis Example 1 and N,N-dimethylformamide (DMF) were mixed in the amounts shown in Table A to give a mixture liquid.

After dissolved by heat, this mixture liquid was introduced into 1 liter 4 necked flask equipped with a reflux condenser, a nitrogen inlet pipe, a thermometer and a stirring device, and dissolved oxygen was removed by nitrogen replacement. Then ammonium persulfate (APS) as an initiator was introduced in the amount shown in Table A. While stirring, a copolymerization reaction was performed at 60 °C for 8 hours, and copolymer (Solution C) was obtained. A glass transition point of the copolymer was 110 °C.

Preparative Example 4

Polymerization of Product 2/MMA copolymer (Solution D)

The same procedure as in Preparative Example 3 was followed to give a copolymer (Solution D) except that Product 2 was used instead of Product 1 used in the Preparative Example 3. The glass transition point of the copolymer was 108 °C.

Preparative Example 5

Polymerization of Product 1/MMA copolymer (Emulsion A)

Product 1 provided with Synthesis Example 1, pure water, n-lauryl mercaptan (LSH), polyoxyethylenealkylphenylether ammonium sulfate (HITENOL N-17, an anionic emulsifier), polyoxyethylenealkylphenyl ether (NONION HS-220, a nonionic emulsifier), polyoxyethylene sorbitan monolaurate (NONION LT-221, a nonionic emulsifier), dipropyleneglycol monomethyl ether (DPM) were mixed in amounts shown in Table A, and mixture liquid was prepared.

After dissolved by heat, the mixture liquid was emulsified with an ultrasonic emulsifier to give an emulsion. The emulsion was introduced into a 1 liter 4 necked flask equipped with a reflux condenser, a nitrogen inlet pipe, a thermometer and a stirring device, and dissolved oxygen was removed by nitrogen replacement. Then ammonium persulfate as initiator (APS) was introduced in the amount shown in Table A. While stirring the copolymerization reaction was performed at 60 °C for 8 hours, and a copolymer (Emulsion A) was obtained. The glass transition point of the copolymer was 109 °C.

Preparative Example 6

Polymerization of Product 2/MMA copolymer (Emulsion B)

The same procedure as in Preparative Example 5 was followed to give a copolymer (Emulsion B) except that Product 2 was used instead of Product 1 used in the Preparative Example

5. The glass transition point of the copolymer was 108 °C.

Comparative Preparative Example 1

Preparation of Product 3/MMA cross-linking precursor (Solution E)

5 The same procedure as in Preparative Example 1 was followed to give Product 3/MMA cross-linking precursor (Solution E) except that Product 3 was used instead of Product 1 used in the Preparative Example 1.

Comparative Preparative Example 2

10 Preparation of Product 4/MMA cross-linking precursor (Solution F)

 The same procedure as in Preparative Example 1 was followed to give Product 4/MMA cross-linking precursor (Solution F) except that Product 4 was used instead of Product 1 used in the Preparative Example 1.

15

Comparative Preparative Example 3

Polymerization of Product 3/MMA copolymer (Solution G)

 The same procedure as in Preparative Example 3 was followed to give a copolymer (Solution G) except that Product 3 was used instead of Product 1 used in the Preparative Example 3. The glass transition point of the copolymer was 165 °C.

20

Comparative Preparative Example 4

Polymerization of Product 4/MMA copolymer (Solution H)

 The same procedure as in Preparative Example 3 was followed to give a copolymer (Solution H) except that Product

25

4 was used instead of Product 1 used in the Preparative Example 3.

Comparative Preparative Example 5

Polymerization of Product 3/MMA copolymer (Emulsion C)

- 5 The same procedure as in Preparative Example 5 was followed to give a copolymer (Emulsion C) except that Product 3 was used instead of Product 1 used in the Preparative Example 5.

Comparative Preparative Example 6

- 10 Polymerization of Product 4/MMA copolymer (Emulsion D)

 The same procedure as in Preparative Example 5 was followed to give a copolymer (Emulsion D) except that Product 4 was used instead of Product 1 used in the Preparative Example 5.

- 15 The type and the amount of materials employed in Preparative Examples 1 to 6 and in Comparative Preparative Examples 1 to 6 are shown in Table A.

Table A

	Preparative Example						Comparative Preparative Example					
	1	2	3	4	5	6	1	2	3	4	5	6
DPM	-	-	-	-	30	30	-	-	-	-	30	30
Pure water	-	-	-	-	401.3	401.3	-	-	-	-	401.3	401.3
LSH	-	-	-	-	3	3	-	-	-	-	3	3
N-17	-	-	-	-	4.5	4.5	-	-	-	-	4.5	4.5
HS-220	-	-	-	-	6	6	-	-	-	-	6	6
LT-221	-	-	-	-	4.5	4.5	-	-	-	-	4.5	4.5
APS	-	-	0.75	0.75	0.75	0.75	-	-	0.75	0.75	0.75	0.75
Product 1	90	-	90	-	90	-	-	-	-	-	-	-
Product 2	-	90	-	90	-	90	-	-	-	-	-	-
Product 3	-	-	-	-	-	-	90	-	90	-	90	90
Product 4	-	-	-	-	-	-	-	90	-	90	-	-
DMF	-	-	450	450	-	-	-	-	450	450	-	-
Methanol	450	450	-	-	-	-	450	450	-	-	-	-
Benzoin methyl ether	0.75	0.75	-	-	-	-	0.75	0.75	-	-	-	-
Methylene bis acrylamide	4	4	-	-	-	-	4	4	-	-	-	-

Example 1

Solution A prepared in Preparative Example 1 was diluted with methanol to give a treatment liquid having a solid content of 3 % by weight.

5 The treatment liquid obtained above was sprayed onto a nylon pile carpet fabric (a blue unbacked product) to give a fluorine concentration of 400 ppm, and then the fabric was exposed to UV light with an ultra high-pressure mercury-vapor lamp for 10 minutes. Compounds included within solid content
10 in the treatment liquid are shown in Table B. Water repellency, oil repellency, stain block property and soil releasability were evaluated for the samples before and after cleaning.

 On the other hand, a coated film was formed on the glass plate top with the treatment liquid. Knoop hardness of the
15 coated film was measured.

Results are shown in Table C.

Example 2

 Solution B prepared in Preparative Example 2 was diluted with methanol to give a treatment liquid having a solid content
20 of 3 % by weight. This treatment liquid was evaluated as in Example 1.

Results are shown in Table C.

Example 3

 Solution C prepared in Preparative Example 3 was diluted
25 with N,N-dimethylformamide (DMF) to give a treatment liquid

having a solid content of 3 % by weight. The treatment liquid obtained above was sprayed onto a nylon pile carpet fabric (a blue unbacked product) to give a fluorine concentration of 400 ppm, and then the fabric was heated and dried at 130 °C for 10 minutes. Water repellency, oil repellency, stain block property and soil releasability were evaluated for the samples before and after cleaning. On the other hand, Knoop hardness of a coated film formed from the treatment liquid was measured.

Results are shown in Table C.

10 Example 4

The Solution D prepared in Preparative Example 4 was diluted with N,N-dimethylformamide (DMF) to give a treatment liquid having a solid content of 3 % by weight. This treatment liquid was evaluated as in Example 3.

15 Results are shown in Table C.

Example 5

The Emulsion A prepared in Preparative Example 5 was diluted with pure water to give a treatment liquid having a solid content of 3 % by weight. The treatment liquid obtained above was sprayed onto a nylon pile carpet fabric (a blue unbacked product) to give a fluorine concentration of 400 ppm, and then the fabric was heated and dried at 130 °C for 10 minutes. Water repellency, oil repellency, stain block property and soil releasability were evaluated for the samples before and after cleaning.

On the other hand, Knoop hardness of a coated film formed from the treatment liquid was measured.

Results are shown in Table C.

Example 6

5 The Emulsion B prepared in Preparative Example 6 was diluted with pure water to give a treatment liquid having a solid content of 3 % by weight. This treatment liquid was evaluated as in Example 5.

Results are shown in Table C.

10 Comparative Examples 1 and 2

Each solution prepared in Comparative Preparative Examples 1 and 2 was diluted with methanol to give a treatment liquid having a solid content of 3 % by weight. These solutions were evaluated as in Example 1.

15 Results are shown in Table C.

Comparative Examples 3 and 4

Each solution prepared in Comparative Preparative Examples 3 and 4 was diluted with N,N-dimethylformamide (DMF) to give a treatment liquids having a solid content of 3 % by weight. These solutions were evaluated as in Example 3.

Results are shown in Table C.

Comparative Examples 5 and 6

Each emulsion prepared in Comparative Preparative Examples 5 and 6 was diluted with pure water to give a treatment liquids having a solid content of 3 % by weight. These solutions

were evaluated as in Example 5.

Results are shown in Table C.

0944835-14801
T08T2T 9E84T660

Table B

		Example						Comparative Example					
		1	2	3	4	5	6	1	2	3	4	5	6
Inorganic component	TMSM	O	O	O	O	O	O	-	O	-	O	-	O
	TEOS	O	O	O	O	O	O	-	O	-	O	-	O
Organic component	PMA	O	O	O	O	O	O	O	-	O	-	O	-
	Fluorine-containing compound	O	O	O	O	O	O	O	-	O	-	O	-
	MMA	O	O	O	O	O	O	O	O	O	O	O	O
Crosslinking agent		O	O	-	-	-	-	O	O	-	-	-	-
Emulsifier		-	-	-	-	O	O	-	-	-	-	O	O

Table C

		Example						Comparative Example					
		1	2	3	4	5	6	1	2	3	4	5	6
Before cleaning	Water repellency	50	50	50	50	50	50	30	0	30	0	30	0
	Oil repellency	3	3	3	3	3	3	2	0	2	0	2	0
	SB property	10	10	10	10	10	10	10	3	10	3	10	3
	Soil releasability (%)	80	80	77	77	77	77	43	29	37	20	37	20
After cleaning (5 times cleaning)	Water repellency	50	50	50	50	50	50	0	0	0	0	0	0
	Oil repellency	3	3	3	3	3	3	0	0	0	0	0	0
	SB property	10	10	10	10	10	10	10	0	10	0	10	0
	Soil releasability (%)	77	77	74	74	74	74	14	0	14	0	14	0
Fluorine residual ratio (%)		95	95	95	95	95	95	5	-	5	-	5	-
Knoop hardness		33	33	30	30	28	28	22	33	10	30	10	29

ADVANTAGES OF THE INVENTION

According to the present invention a surface treatment agent comprising an organic-inorganic hybrid material which imparts a durability maintaining sufficient water repellency, oil repellency, stain block property and soil releasability before and after cleaning.

CLAIMS

1. A surface treatment agent, wherein, when a fiber for carpet
is treated with the surface treatment agent, the treated fiber
5 has following characteristics (1) and (2):

(1) a stain block property of at least 8, in a stain block
examination according to AATCC-TM-175-1993; and

(2) a Knoop hardness (KH) of the surface treatment agent
of at least 5.

10

2. A surface treatment agent comprising:

(A) a metal alkoxide;

(B) a fluorine-containing compound containing a
functional group reactive with the metal alkoxide; and

15

(C) a reactive group-containing polymer having a reactive
group reactive with a substrate to be treated.

20

3. The surface treatment agent according to Claim 2, wherein
a number of alkoxy groups in the metal alkoxide is from 1 to
12.

4. The surface treatment agent according to Claim 2, wherein
a metal in the metal alkoxide (A) is selected from the group
consisting of Si, Ti, Al, Zr, Sn and Fe.

25

5. The surface treatment agent according to Claim 2, wherein the functional group in the fluorine-containing compound (B) is a reactive group selected from the group consisting of a carboxyl group or salt thereof, a sulfonic acid group or salt thereof, a hydroxy group, an epoxy group, a phosphoric group, an alkoxy silane group, a halogenated silyl group, an isocyanate group and a blocked isocyanate group.

6. The surface treatment agent according to Claim 2, wherein the reactive groups in the reactive group-containing polymer (C) are the reactive groups selected from the group consisting of a carboxyl group or a salt thereof, a hydroxy group, an epoxy group, a phosphoric group, an alkoxy silane group, an imine group, a sulfonic group, an amino group, an isocyanate group and a blocked isocyanate group.

7. The surface treatment agent according to Claim 2, wherein the reactive group-containing polymer (C) is a polymer having:

(i) a reactive group selected from the group consisting of a carboxyl group or a salt thereof, a hydroxy group, an epoxy group, a phosphoric group, an alkoxy silane group, an imine group, a sulfonic group, an amino group, an isocyanate group and a blocked isocyanate group; and

(ii) a fluoroalkyl group.

8. The surface treatment agent according to Claim 2, wherein the substrate to be treated is one selected from the group consisting of wood, metal, stone, plastics, concrete and glass.

5 9. An organic-inorganic hybrid material comprising:

(A) a metal alkoxide,

(B) a fluorine-containing compound having a functional group reactive with the metal alkoxide; and

10 (C) a reactive group-containing polymer having a reactive group reactive with a substrate to be treated.

Declaration and Power of Attorney for Patent Application

特許出願宣言書及び委任状

Japanese Language Declaration

日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

As a below named inventor, I hereby declare that:

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

My residence, post office address and citizenship are as stated next to my name,

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者(下記の氏名が一つの場合)もしくは最初かつ共同発明者であると(下記の名称が複数の場合)信じています。

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

SURFACE TREATMENT AGENT COMPRISING

ORGANIC-INORGANIC HYBRID MATERIAL ✓

上記発明の明細書(下記の欄でX印がついていない場合は、本書に添付)は、

the specification of which is attached hereto unless the following box is checked:

☐ ____月 ____日に提出され、米国出願番号または特許協定条約

☒ was filed on February 29, 2000 ✓
as ~~United States Application Number~~ XXXX
PCT International Application Number

国際出願番号を ____ とし、

PCT/JP00/01170 ✓ and was amended on

(該当する場合) ____ に訂正されました。

____ (if applicable).

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

私は、連邦規則法典第37編第1条56項に定義されたとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

Japanese Language Declaration

(日本語宣言書)

私は、米国法典第35編第119条(a)-(d)項又は第365条(b)項に基づき下記の、米国以外の国の少なくとも一カ国を指定している特許協力条約第365条(a)項に基づく国際出願、又は外国での特許出願もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張している本出願の前に出願された特許または発明者証の外国出願を以下に、枠内をマークすることで、示しています。

Prior Foreign Applications

外国での先行出願

57100/1999 ✓ (Number) (番号)	Japan ✓ (Country) (国名)
_____ (Number) (番号)	_____ (Country) (国名)
_____ (Number) (番号)	_____ (Country) (国名)

私は、第35編米国法典119条(e)項に基づいて下記の米国特許出願規定に記載された権利をここに主張致します。

_____ (Application No.) (出願番号)	_____ (Filing Date) (出願日)
--------------------------------------	---------------------------------

私は、下記の米国法典第35編第120条に基づいて下記の米国特許出願に記載された権利、又は米国を指定している特許協力条約第365条(c)に基づく権利をここに主張します。又、本出願の各請求範囲の内容が米国法典第35編第112条第1項又は特許協力条約で規定された方法で先行する米国特許出願に開示されていない限り、その先行米国出願書提出日以降で本出願書の日本国内又は特許協力条約国際出願提出日までの期間中に入手された、連邦規則法典第37編第1条第56項で定義された特許資格の有無に関する重要な情報について開示義務があることを認識しています。

_____ (Application No.) (出願番号)	_____ (Filing Date) (出願日)
_____ (Application No.) (出願番号)	_____ (Filing Date) (出願日)

私は、私自身の知識に基づいて本宣言中で私が行う表明が真実であり、かつ私の入手した情報と私の信ずるところに基づく表明が全て真実であると信じていること、さらに故意になされた虚偽の表明及びそれと同等の行為は米国法典第18編第1001条に基づき、罰金または拘禁、もしくはその両方により処罰されること、そしてそのような故意による虚偽の声明を行えば、出願した、又は既に許可された特許の有効性が失われることを認識し、よってここに上記のごとく宣誓を致します。

I hereby claim foreign priority under Title 35, United States Code, Section 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority Not Claimed

優先権主張なし

4/March/1999 ✓ (Day/Month/Year Filed) (出願年月日)	<input type="checkbox"/>
_____ (Day/Month/Year Filed) (出願年月日)	<input type="checkbox"/>
_____ (Day/Month/Year Filed) (出願年月日)	<input type="checkbox"/>

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

_____ (Application No.) (出願番号)	_____ (Filing Date) (出願日)
--------------------------------------	---------------------------------

I hereby claim the benefit of Title 35, United States Code Section 120 of any United States application(s), or 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code Section 112, I acknowledge the duty to disclose any material information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

_____ (Status: Patented, Pending, Abandoned) (現況: 特許許可済、係属中、放棄済)
_____ (Status: Patented, Pending, Abandoned) (現況: 特許許可済、係属中、放棄済)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Japanese Language Declaration

(日本語宣言書)

委任状: 私は、下記の発明者として、本出願に関する一切の手続きを米国特許商標局に対して遂行する弁理士又は代理人として、下記のことを指名致します。(弁理士、又は代理人の氏名及び登録番号を明記のこと)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (list name and registration number)

John H. Mion, Reg. No. 18,879; Thomas J. Macpeak, Reg. No. 19,292; Robert J. Seas, Jr., Reg. No. 21,092; Darryl Mexic, Reg. No. 23,063; Robert V. Sloan, Reg. No. 22,775; Peter D. Olexy, Reg. No. 24,513; J. Frank Osha, Reg. No. 24,625; Waddell A. Biggart, Reg. No. 24,861; Louis Gubinsky, Reg. No. 24,835; Neil B. Siegel, Reg. No. 25,200; David J. Cushing, Reg. No. 28,703; John R. Inge, Reg. No. 26,916; Joseph J. Ruch, Jr., Reg. No. 26,577; Sheldon I. Landsman, Reg. No. 25,430; Richard C. Turner, Reg. No. 29,710; Howard L. Bernstein, Reg. No. 25,665; Alan J. Kasper, Reg. No. 25,426; Kenneth J. Burchfiel, Reg. No. 31,333; Gordon Kit, Reg. No. 30,764; Susan J. Mack, Reg. No. 30,951; Frank L. Bernstein, Reg. No. 31,484; Mark Boland, Reg. No. 32,197; William H. Mandir, Reg. No. 32,156; Scott M. Daniels, Reg. No. 32,562; Brian W. Hannon, Reg. No. 32,778; Abraham J. Rosner, Reg. No. 33,276; Bruce E. Kramer, Reg. No. 33,725; Paul F. Neils, Reg. No. 33,102 and Brett S. Sylvester, Reg. No. 32,765

書類送付先:

Send Correspondence to:

SUGHRUE, MION, ZINN, MACPEAK & SEAS, PLLC
2100 Pennsylvania Avenue, N.W., Washington, D.C. 20037-3202

直通電話連絡先: (名称及び電話番号)

Direct Telephone Calls to: (name and telephone number)

(202)293-7060

唯一又は第一発明者名	1-00	Full name of sole or first inventor	Kazuyuki SATO
発明者の署名	日付	Inventor's signature	Date
		Kazuyuki SATO	Sep. 6, 2001
住所		Residence	
		Settsu-shi, Osaka, Japan	JPX
国籍		Citizenship	
		Japan	✓
郵便の宛先		Post office address	
		c/o Yodogawa Works of DAIKIN INDUSTRIES,	
		LTD., 1-1, Nishihitotsuya, Settsu-shi,	
		Osaka 566-8585 Japan	
第二共同発明者名 (該当する場合)	2-00	Full name of second joint inventor, if any	Masamichi MORITA
第二発明者の署名	日付	Second inventor's signature	Date
		Masamichi Morita	Sep. 5, 2001
住所		Residence	
		Settsu-shi, Osaka, Japan	JPX
国籍		Citizenship	
		Japan	✓
郵便の宛先		Post office address	
		c/o Yodogawa Works of DAIKIN INDUSTRIES,	
		LTD., 1-1, Nishihitotsuya, Settsu-shi,	
		Osaka 566-8585 Japan	

(第三以降の共同発明者についても同様に記載し、署名をする (Supply similar information and signature for third and subsequent joint inventors.)

Japanese Language Declaration
(日本語宣言書)

第三共同発明者名 (該当する場合) <div style="text-align: right; margin-top: 10px;">3-00</div>	Full name of third joint inventor, if any <u>Fumihiko YAMAGUCHI</u>
第三発明者の署名 <div style="text-align: right; margin-top: 10px;">日付</div>	Third inventor's signature <u>Fumihiko Yamaguchi</u>
住所	Date <u>Sep. 5, 2001</u> Residence <u>Settsu-shi, Osaka, Japan JPX</u>
国籍	Citizenship <u>Japan</u>
郵便の宛先	Post office address <u>c/o Yodogawa Works of DAIKIN INDUSTRIES,</u> <u>LTD., 1-1, Nishihitotsuya, Settsu-shi,</u> <u>Osaka 566-8585 Japan</u>
第四共同発明者名 (該当する場合) <div style="text-align: right; margin-top: 10px;">4-00</div>	Full name of fourth joint inventor, if any <u>Motonobu KUBO</u>
第四発明者の署名 <div style="text-align: right; margin-top: 10px;">日付</div>	Fourth inventor's signature <u>Motonobu Kubo</u>
住所	Date <u>Sept. 6, 2001</u> Residence <u>Settsu-shi, Osaka, Japan JPX</u>
国籍	Citizenship <u>Japan</u>
郵便の宛先	Post office address <u>c/o Yodogawa Works of DAIKIN INDUSTRIES,</u> <u>LTD., 1-1, Nishihitotsuya, Settsu-shi,</u> <u>Osaka 566-8585 Japan</u>
第五共同発明者名 (該当する場合)	Full name of fifth joint inventor, if any
第五発明者の署名 <div style="text-align: right; margin-top: 10px;">日付</div>	Fifth inventor's signature Date
住所	Residence
国籍	Citizenship
郵便の宛先	Post office address
第六共同発明者名 (該当する場合)	Full name of sixth joint inventor, if any
第六発明者の署名 <div style="text-align: right; margin-top: 10px;">日付</div>	Sixth inventor's signature Date
住所	Residence
国籍	Citizenship
郵便の宛先	Post office address